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Published in:
Journal of Physics%3A Condensed Matter

DOI:
[10.1088/0953-8984/3/39/011](https://doi.org/10.1088/0953-8984/3/39/011)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1991

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Citation for published version (APA):

Leuken, H. V., & Groot, R. A. D. (1991). Ab initio electronic-structure calculations on the Nb/Cu multilayer system. *Journal of Physics%3A Condensed Matter*, 3(39). <https://doi.org/10.1088/0953-8984/3/39/011>

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Ab initio electronic-structure calculations on the Nb/Cu multilayer system

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Received 13 May 1991

Abstract. *Ab initio* electronic-structure calculations are reported for coherent and incoherent Nb/Cu multilayers. An incoherent unit cell describing three Nb BCC (110) layers and three Cu FCC (111) layers is constructed for the layers in the Nishiyama-Wasserman orientation and with relaxed atomic positions at the interface. It is found that the total density of states is a combination of the broadened DOS curves of the parent metals and that at the interface Nb has a decreased, and Cu has an increased, density of states at the Fermi energy. These results are in agreement with experimental results and for Nb can be explained by a broadening of the density of states.

Possible coherency for small modulation wavelengths is investigated by calculating the total energies for overall BCC [110] and overall FCC [111] Nb/Cu multilayers consisting of one layer of each metal and comparing these with the total energy results of the incoherent structure. The positive interface energy found for the Nb/Cu system favours the incoherent multilayer over the coherent multilayers, where a positive structural energy is also involved.

1. Introduction

Nb/Cu is one of the best-studied artificial compositionally modulated structures in the relative short history of metallic multilayers (ML). The properties studied since the first report on this system by Schuller [1] in 1908 include elasticity [2-4], the superconducting transition temperature T_c [5] and the upper critical field H_{c2} [6]. In particular in experiments and theories on the dimensional crossover of the temperature dependence of the upper critical field the Nb/Cu system has played an important role. Structural studies [1, 7] have indicated that the Nb/Cu ML comprises Nb BCC (110) and Cu FCC (111) layers with both elements retaining the values of the bulk lattice parameter. The combination of these dissimilar structures makes the Nb/Cu ML system a clear example of an ML that is incoherent in the modulation direction. Despite the wealth of experimental information that exists on this system, very little is known either experimentally or theoretically about its electronic structure.

In preparation for future research on the interpretation of superconducting properties on the basis of calculated electronic structures employing the formalism of Takahashi and Tachiki [8] we present here electronic-structure calculations for the Nb/Cu

ML system. We have used the localized spherical wave (LSW) [9] method for performing the calculations. To that end a unit cell model for the incoherent Nb/Cu ML was devised. The way in which this was done is described in section 2. Candidates for a possible coherent Nb/Cu ML structure are also described in this section along with the structures of reference systems facilitating the interpretation of the ML results. In section 3 the computational details are given. In section 4 the results are presented. Concluding remarks are made in section 5.

2. Structure

In spite of the many experiments on the Nb/Cu ML system, detailed knowledge of the structure is still not available. For large modulation wavelengths, Λ , it has been established [1,7] that the metals are ordered as Nb (110) and Cu (111) layers with elemental lattice spacings of 3.30 and 3.61 Å respectively. For a Λ of about 20 Å, an order-disorder transition is observed, and for smaller Λ , x-ray diffraction experiments show one broad peak indicating a large distribution of the interatomic spacings. Experimental details on the relative orientation of the FCC and BCC planes and the precise quality of the modulation of the composition are not, as far as we know, yet available. Probably such studies are complicated by the grain-like nature of the Nb/Cu multilayers. The grains exhibit a wire texture and are oriented randomly around the normal of the layers [7, 10]. The Nb-Cu phase diagram shows a maximal mutual solubility of the metals of only 4% [5]. Furthermore it was found [10] that very little interdiffusion occurs once the ML samples are prepared and that the Nb/Cu interface width is restricted to two interatomic planes [11]. In the current work interdiffusion is neglected.

It must be clear from this that there is no clear choice for an incoherent Nb/Cu unit cell and that we had to construct one. In doing so, the constraints were that this cell must contain both Nb and Cu in their elemental structures, or a good approximation to these structures, and, for economy, that the cell should not contain too many atoms per layer. A procedure for accomplishing this was given in an earlier study on Nb/Zr ML structures [9]. It can be summarized as follows.

(i) The translational vectors perpendicular to the modulation direction that describe both the Nb and Cu atoms in the planes must be found. These vectors determine the number of atoms per layer.

(ii) A commensurate match between BCC (110) and FCC (111) layers is impossible. They are incommensurate or at best partially commensurate. This implies that the elemental BCC and FCC structures have to be deformed if the metals are to be combined into one unit cell. The deformation has to be chosen so as to render the smallest possible effects on the electronic structure.

(iii) The unit cell is constructed by stacking (distorted) BCC (110) and FCC (111) layers.

(iv) Finally, a model for the relaxation at interface has to be devised.

There are a number of interesting studies [12-16] on the epitaxial energy of FCC (111) on BCC (110) layers. The possible commensuration of these layers has been investigated as a function of the lattice parameter ratio of adsorbate and substrate, relative positions and orientations of the layers. For a given ratio, energetically preferred orientations emerge. These can provide useful guides in determining the lattice

vectors perpendicular to the modulation direction. The ratio of the lattice parameters of Cu and Nb is 1.09, which is close to a preferred ratio in the Nishiyama-Wasserman (NW) orientation. In this orientation there is commensuration between the FCC [112] and the BCC [110] directions. The in-layer spacings in these directions satisfy $a_{\text{Cu}}\sqrt{1.5} = a_{\text{Nb}}\sqrt{2}$, and the ratio is 1:15. This is the C(x;1) orientation of [13]. Note that in this situation there is no commensuration between other low index directions. For instance along the directions perpendicular to the commensurate directions, the BCC [001] and FCC [110] directions, the in-layer spacings are related by $a_{\text{Nb}} = \frac{1}{2}\sqrt{2}a_{\text{Cu}}$. (This is the C(y;1) orientation of [13].) For this reason such a situation is commonly referred to as axially commensurate. Axial commensuration is the best possible match between FCC (111) and BCC (110) planes because the in-plane distances prevent overall commensuration.

The lattice vectors in the (x, y) plane, perpendicular to the modulation direction, are defined as the independent vectors which point to positions common to a Nb and a Cu atom, the origin also being a common position. We started looking for such positions with the layers in the NW orientation. For $3a_{\text{Nb}}$ and $2\sqrt{2}a_{\text{Cu}}$ there is a close match in the BCC [001] direction which differs by 0.31 Å. This position combined with the corresponding positions $(3\frac{1}{2}, \sqrt{\frac{1}{2}})a_{\text{Nb}}$ and $(2\frac{1}{4}\sqrt{2}, \sqrt{\frac{3}{8}})a_{\text{Cu}}$ results in a cell with three Nb and four Cu atoms per layer. The mismatch between the latter positions is (0.06, 0.12) Å. An attempt was made to obtain similar small cells with a better positional match by considering deviations from the NW orientation. Rotating the planes around the z-direction only yielded cells with 12 or more atoms per layer. In this procedure the angle ϕ between the commensurate directions of the NW orientation was varied in 300 steps between 0 and $\pi/6$ rad keeping the lattice parameters of Cu, a_{Cu} , and of Nb, a_{Nb} , fixed. The absolute tolerance of the positional match was taken to be 0.1 Å.

Averaging the positional vectors of Nb and Cu for the two matching situations results in the vectors $V_1 = (10.0553, 0.0)$ and $V_2 = (11.5185, 2.271)$. The vector V_2 is redefined as $V_2 - V_1$ giving $V_2 = (1.463, 2.2721)$. For this cell we have axial commensuration in the y-direction and forced commensuration in the x-direction where three Nb distances are commensurate with four Cu distances, giving seven atoms per Nb/Cu bilayer. We note that this is close to the C(x;1) orientation of [13], where the definition of -x and -y axes are interchanged. Because the NW lattice parameter ratio is not perfectly satisfied for Nb and Cu and we have forced commensuration the elemental crystal structures are distorted in the incoherent ML unit cell.

The continuation in the modulation direction is made by stacking the metal layers according to the way in which they are stacked in the elemental metals. For the Nb part this is an 'AB' stacking such as $(\frac{1}{2}, 0, \Delta z_{\text{Nb}}/a_{\text{Nb}})$ and for Cu an 'ABC' stacking such as $(\frac{1}{3}, \frac{2}{3}, \Delta z_{\text{Cu}}/a_{\text{Cu}})$. The interlayer distances, Δz , were determined by keeping at least one nearest-neighbour distance across the layers the same as in the elemental metals. The distances found in this way, 2.3212 Å for Nb and 2.0681 Å for Cu, were very close to the bulk interlayer distances $\frac{1}{2}\sqrt{2}a_{\text{Nb}}$ and $\frac{1}{3}\sqrt{3}a_{\text{Cu}}$.

The effect of the lattice distortion on the electronic structure was investigated by calculating the structures of Nb and Cu in the bulk deformed crystal according to the constructed incoherent ML. These structures, which will be called 1:0 and 0:1 respectively, are both triclinic with one atom per unit cell (space group C_i^1 , number 2 in the *International Tables* [17] (IT)). They are to be compared with the elemental metals BCC Nb, O_h^8 and FCC Cu, O_h^5 , which were also calculated. The distortion

caused a splitting of the Nb and Cu energy levels that are degenerate in the centre Γ of the Brillouin zone (BZ) of the elemental metals. At the next energies above the s-band in Γ , the metals Nb and Cu have a threefold (t_{2g}) and a twofold (e_g) degenerate level. In Cu these two degenerate levels are well below the Fermi energy and therefore we will ignore their splitting but in Nb the triply degenerate level is only 0.5 eV above the Fermi level. Splitting of this level can result in changes in the shape of the Fermi surface. Indeed, calculating Nb in the 1:0 structure results in a splitting of the levels in Γ , shifting one band below the Fermi energy. A simple averaging of the matching positions of Nb and Cu turns out to be too crude for the Nb part of the ML. In order to improve upon this we use the freedom that is given in the imperfect match and take as a second choice for the in-layer vectors a 2:1 averaging of the Nb compared with the Cu positions. In this case the ML structure is closer to the elemental Nb structure, but the Cu part is worse. The Nb in this ML structure still shows split levels, but the lowest level of the previously degenerate levels stays above the Fermi energy. From now on the cell obtained by the 2:1 averaging of the Nb and Cu positions will be used. The lattice vectors become $V_1 = (10.0035, 0.0)$ and $V_2 = (1.5234, 2.2925)$.

The final step in the determination of the ML unit cell is the relaxation of the atoms at the Nb/Cu interface. This was done in a manner previously presented [9], based on a procedure to obtain a similar overlap of Wigner-Seitz (WS) spheres at the interface as in the bulk-like parts of the constituent metals, while the unlike atoms are optimized to have an overlap that is the average of the bulk-like overlaps. We use the following input parameters. The WS radii R_{WS} of the metals are 1.4146 Å for Cu and 1.6180 Å for Nb. From the R_{WS} of the elemental metals Cu (1.4108 Å) and Nb (1.6248 Å) it follows that in the incoherent ML Cu has a somewhat larger volume and Nb has a somewhat smaller volume. The equilibrium overlap distances d_R , defined as the difference between the sum of the R_{WS} of the two WS spheres and the distance between their centres, were taken as 0.2632 Å for Cu and 0.3886 Å for Nb. An Nb/Cu interface with inversion symmetry and a c-axis of 13.1679 Å was taken as the input structure for this procedure. This c-axis is three times the interlayer distance of Nb plus three times the interlayer distance of Cu. It is the length of the V_3 vector that points in the z-direction. By this procedure the interface distance is the average of the Nb and Cu interlayer distances. The Nb interface layers have an atom placed at the origin and in the 'ABC' stacking of the Cu layers the central 'B' layer also has an atom at the origin. The inversion symmetry is maintained throughout the procedure and leaves the Cu slab fixed between the Nb slabs. Only the interface atoms move and the final result is also symmetrical inversion. The largest WS sphere overlap no longer occurs across the Nb-Cu interface but between Nb spheres which are connected by the vector V_2 . The shared volume is only 3.2% of the volume of a Nb sphere.

The final Nb/Cu 3:3 unit cell for the incoherent multilayer has space group C_{1i}^1 , number 2 in the IT, with 21 atoms in 14 classes. The atomic positions relative to the lattice vectors $\{V_i\}$ are given in table 1. The positions inside the unit cell, projected in the (x, y) plane, are also shown in figure 1.

The inter-layer distance at the interface becomes wider which is an effect of the interface relaxation procedure. This is mainly due to the Nb atoms, whose change in average z-direction is more than ten times larger than that of the Cu interface atoms.

Two other coherent structures were also considered besides the incoherent structure. The first one consists of an alternate stacking of Nb and Cu both ordered in FCC (111) layers. This rhombohedral system, described by the space group D_{3d}^5 , number 166 in the IT, will be referred to as NbCu FCC. This structure was calculated with

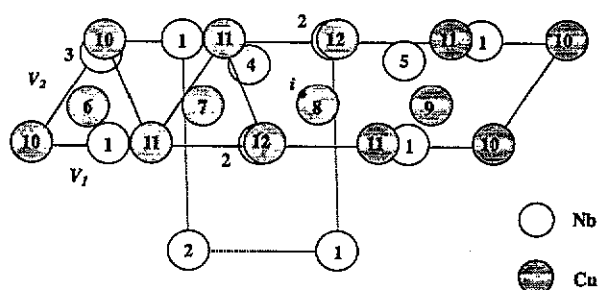


Figure 1. Atomic positions of Nb and Cu projected in the (x, y) plane inside the incoherent Nb/Cu 3:3 unit cell which is defined in this plane by the lattice vectors V_1 and V_2 . The atoms are labelled according to the different classes of table 1. The full lines between the Cu positions with labels 10, 11 and 12 show part of the distorted FCC (111) plane. The broken lines between the Nb positions indicate part of the BCC (110) plane. The label 'i' indicates the inversion centre.

three different lattice parameters, a_{Cu} , and with the values increased by 2 and 10%. The second structure consists of an overall stacking of BCC (110) layers, alternatingly formed by Nb and Cu atoms. This CFC orthorhombic system is described by the space group D_{2h}^{19} , number 65 in the IT, and will be referred to as NbCu BCC. It was calculated with only one lattice parameter, that of elemental Nb, a_{Nb} .

Table 1. Relative positions of the atoms in the different classes for the incoherent Nb/Cu 3:3 multilayer.

| Class | | x | y | z |
|------------|----|--------|--------|--------|
| Nb bulkl. | 1 | 0.1667 | 0.0000 | 0.0000 |
| | 2 | 0.5000 | 0.0000 | 0.0000 |
| Nb interf. | 3 | 0.0179 | 0.9151 | 0.1713 |
| | 4 | 0.3659 | 0.7725 | 0.1693 |
| | 5 | 0.6908 | 0.8219 | 0.1665 |
| Cu interf. | 6 | 0.0713 | 0.3474 | 0.3439 |
| | 7 | 0.3205 | 0.3573 | 0.3426 |
| | 8 | 0.5702 | 0.3594 | 0.3432 |
| | 9 | 0.8216 | 0.3500 | 0.3439 |
| Cu bulkl. | 10 | 0.0000 | 0.0000 | 0.5000 |
| | 11 | 0.2500 | 0.0000 | 0.5000 |
| | 12 | 0.5000 | 0.0000 | 0.5000 |

3. Calculations

Ab initio, self-consistent, localized-spherical-wave (LSW) calculations [9] using a scalar-relativistic Hamiltonian were carried out. We used local-density exchange-correlation potentials inside the space filling, and therefore overlapping, spheres around the atoms. All electrons were included in the self-consistent calculations.

In the iterated procedure a modified Broyden method [18] for accelerated convergence was used and the k -points were distributed uniformly in an irreducible part of the first Brillouin zone (BZ). A distribution corresponding to a volume of BZ per k -point

of the order of $4.9 \times 10^{-5} \text{ \AA}^{-3}$ for the incoherent system was used. When the system was close to convergence the density of k -points was increased to $2.9 \times 10^{-6} \text{ \AA}^{-3}$. The volume per k -point used for the other systems was 10^{-5} \AA^{-3} at most. Self-consistency was assumed when the changes in the local partial charges in each atomic sphere decreased to the order of 10^{-4} . Subsequently the densities of states were constructed by solving the Hamiltonian for the same density of k -points and sampling the eigenvalues in a histogram of 300 channels each with a width of 4.33 mRyd.

In constructing the LSW basis, the spherical waves were augmented by solutions of the scalar-relativistic radial equations indicated by the atomic-like symbols 5s, 5p, 4d and 4s, 4p, 3d corresponding to the valence levels of the parent metals Nb and Cu respectively. The internal l -summation, used to augment the central Hankel function at surrounding atoms, was extended to $l = 3$, resulting in the use of 4f orbitals for Nb and for Cu.

The BCC-based structures have typical screening cluster sizes of fifteen atoms, consisting of a central atom and two neighbouring shells, one with eight and one with six atoms, giving 126 degrees of freedom for screening the central Hankel functions. The FCC-based structures have shells of twelve and six atoms, resulting in 162 degrees of freedom. The screening clusters for the atoms in the incoherent ML have values between these extremes and consist of seventeen or eighteen atoms giving 144 or 153 degrees of freedom.

4. Results

In the following subsections we present the results for the incoherent Nb/Cu ML in the form of density of states curves (4.1) and the magnitude of the density of states at the Fermi energy (4.2) and compare them with the results of the elemental metals and those of the Nb 1:0 and Cu 0:1 systems. In subsection 4.3 the energies of these systems are discussed together with the energy results for the coherent BCC and FCC multilayers.

4.1. Density of states

The total and layer-resolved density of states (DOS) curves of the incoherent Nb/Cu 3:3 ML are given in figure 2. Only one class from the classes within a layer is given. The other classes do not differ significantly from the ones presented.

The Nb/Cu 3:3 total DOS of figure 2(a) can be divided in three different energy regions. The most pronounced region extends from -5.5 to -2 eV and is characterized by a collection of peaks that dominate the DOS. At smaller energies, from -5.5 eV downwards to about -9.5 eV the DOS is flat and smoothly decreasing. From -2 eV to above the Fermi level the DOS is also constant but the density is higher than in the low energy region. There are some small peaks in the high energy region at about 0.7, 3.3, 3.9 and 4.9 eV.

Using the other panels of figure 2 the different regions can be easily ascribed to the constituent metals. The low energy region is due almost exclusively to Cu states and in the region from -5.5 to -2 eV the peaks are also clearly of Cu origin. Nb also has a state density in the latter region but it has considerable less structure than Cu. The effect of the Nb states can be seen as an increase in the intensity of the DOS without any alteration in the shape determined by Cu. For the states above -2 eV the build-up of the DOS is exactly the opposite. Here the Nb states are responsible for

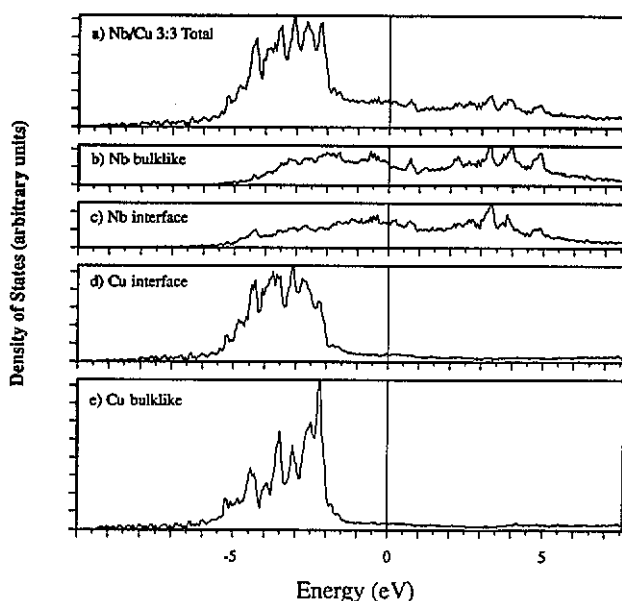


Figure 2. Density of states curves for the (a) Nb/Cu 3:3 multilayer and a representative curve for the atoms in the different layers, (b) Nb-bulk-like, (c) Nb-interface, (d) Cu-interface and (e) Cu-bulk-like. The horizontal axis is in electronvolts (eV) relative to the Fermi energy and the vertical axis is in arbitrary units.

the structure and the flat Cu states merely add to the total density without altering the shape.

Before discussing the layer-resolved DOS curves of the incoherent ML we consider figure 3, in which the DOS curves of the elemental metals and the metals in the ML crystal structure, Nb 1:0 and Cu 0:1, are presented. From this figure the effect of the multilayer structure on the DOS curves of the elemental metals can be seen. The 1:0 and 0:1 curves still bear a fair resemblance to the curves of the elemental metals. This is a further indication that the distortions of the FCC and BCC structures are not too severe. The most striking differences are observed for the sharpest peaks and can be identified as broadening. The distortion of the BCC and FCC lattices has raised the degeneracies of the levels, as was discussed in section 2, and there are some corresponding changes in the dispersion of the bands. As a consequence the peaks that are sharp in the bulk Nb and Cu appear broadened in the 1:0 and 0:1 systems.

The layer-resolved DOS curves in figure 2 are still different from the 1:0 and 0:1 results because here the atoms have different environments caused by the multilayering. Their environments have suffered both chemical and structural changes because of the (relaxed) interface. The effect that this has on the DOS of the different layers of the incoherent ML will now be discussed.

If we consider the sequence of DOS curves for Nb (figure 3(a)), Nb 1:0 (figure 3(b)) and the layer-resolved curves of Nb in the ML (figures 2(b) and (c)), the effect of increased broadening strongly emerges. The broadening effects are clearly stronger in the ML than in the 1:0 structure which is not surprising from the earlier discussion. The Nb curves of figures 2(b) and (c) look very much alike. This similarity is ascribed to the small modulation wavelength and the open structure of the BCC (110) layers which cause a relatively small difference between the environment of the interface and

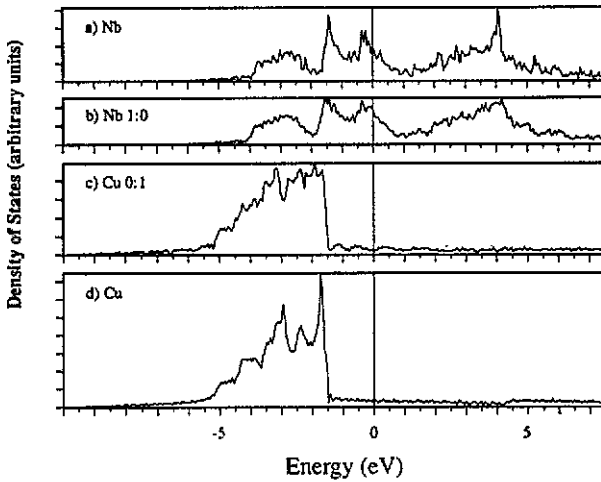


Figure 3. Density of states curves for (a) elemental BCC Nb, (b) Nb in the multilayer crystal structure, denoted as Nb 1:0, (c) Cu in the multilayer crystal structure, denoted as Cu 0:1 and (d) elemental FCC Cu. Axes are as in figure 2.

the bulk-like layers. There are some small differences: for instance the Nb interface DOS has a somewhat lower density in the -3.5 to -1.5 eV region and there is some difference in the peaks around about 4 eV. Note also the appearance of a small peak at -4.4 eV in figure 2(c) which causes an extension towards the lower energies of the Nb-interface DOS curve in the ML. This peak has a large counterpart in the DOS curves of the Cu layers and is a sign of Nb-Cu interaction.

What is striking about the different Cu DOS curves is that elemental Cu (figure 3(d)) compared with Cu 0:1 (figure 3(c)) is quite similar in manner to bulk-like Cu (figure 2(e)) compared with Cu interface (figure 2(d)). The appearance of sharp peaks in the bulk-like Cu DOS is thought to have its origin in the interface relaxation process. The Cu atoms in the bulk-like layer have exactly the same in-layer positions as the Cu atoms in the Cu 0:1 basal plane, the distorted FCC (111) layer. However, the close-packed nature of this layer causes the interface atoms in the relaxation procedure to be centred over this layer, whereas in the 0:1 structure they are positioned according to the $(\frac{1}{3}, \frac{2}{3})$ stacking. In this latter stacking the smallest deviation from the average interatomic distance is about twice as large as the largest deviation for the relaxed interface. We note that there is a shift of 0.5 eV in the positions of the peaks at their onset. In both ML Cu DOS curves the peaks start at -2 eV whereas in the Cu and Cu 0:1 DOS they start at -1.5 eV.

4.2. DOS at the Fermi energy

The Nb/Cu system has been the subject of recent detailed studies on the dimensional crossover of the temperature dependence of the critical field in the proximity of coupled multilayers [6, 8, 11, 19, 20]. In the theoretical description of this phenomenon [8], as well as for the calculation of the superconducting transition temperature T_c [5, 21], the electronic density of states at the Fermi level, $N(E_F)$, is an important parameter. The value of $N(E_F)$ as an input parameter is usually taken to be the bulk value and this is kept constant for the different layers of one metal in the multilayer. In our calculation we studied the behaviour of $N(E_F)$ across the layers and tried to learn

about the mechanisms that alter the DOS at E_F from the bulk values.

The $N(E_F)$ values, given in table 2, were determined from the DOS results by linearly interpolating between the DOS values of the two histogram energies adjacent to the Fermi energy. The results for the different layers of the ML are the average values of the $N(E_F)$ of the atoms in the layers.

Table 2. Densities of states at the Fermi energy E_F in states per Rydberg-atom.

| | |
|--------------|------|
| Nb BCC | 19.4 |
| Nb 1:0 | 19.1 |
| Nb bulk-like | 13.5 |
| Nb interface | 17.4 |
| Cu interface | 4.8 |
| Cu bulk-like | 4.0 |
| Cu 0:1 | 2.6 |
| Cu FCC | 4.6 |
| Nb/Cu 3:3 | 9.2 |

The $N(E_F)$ values of the elements are of the same order as those calculated by Moruzzi *et al* [22], which are 19.0 for Nb and 3.9 for Cu. These smaller values could be partially due to the smaller lattice constants which were used in their calculations. The agreement for Nb is good but the difference for Cu needs some further comment. The histogram sampling method we use for the eigenvalues has the advantage that it is easily implemented for different crystal structures, but a disadvantage is that it is not very efficient. Unless a high k -point density is used when constructing the DOS this method can produce considerable noise, especially for energy bands with large dispersion. In the case of FCC Cu, although 2255 k -points inside an irreducible part of the first BZ were used, corresponding to a volume of $3.5 \times 10^{-6} \text{ \AA}^{-3}$ per k -point, noise is still seen around the Fermi energy in figure 3(d). This noise is believed to be the main cause for the overestimation of the $N(E_F)$ of Cu. In the case of an approximately linear energy dependence of the density of states around E_F on which the noise is superimposed, $N(E_F)$ can be determined by averaging the values of the histogram channels that are symmetrically distributed around E_F . Increasing the number of histogram channels for the determination of $N(E_F)$ of Cu FCC gives a value of 3.8 when four to eight channels are used and a value of 3.9 for up to 16 channels. In the latter case the averaging is over an energy region of about 1 eV.

Comparing the $N(E_F)$ values which correspond to figure 3, we observe close values for Nb BCC and Nb 1:0, which is the structurally biased component in the construction of the incoherent cell. However, the $N(E_F)$ of Cu decreases when forced into the Cu 0:1 structure. There is also noise in the Cu 0:1 DOS but since this noise is of the order of 0.5 states/Ryd atom it cannot explain the low value of $N(E_F)$. Turning to the results for the layers in the incoherent ML we observe that both Nb layers have a lower $N(E_F)$. The decrease is relative to the elemental as well as the Nb 1:0 $N(E_F)$. The lowering is the clear effect of the broadening of the Nb DOS curves. The difference between the Nb-bulk-like and the Nb-interface result is caused by the different interaction these layers have with Cu. The Cu-interface $N(E_F)$ is higher than both the Cu 0:1 and Cu FCC results due to the covalent interaction with the neighbouring Nb states but

for Cu-bulk-like the result is less clear. Its $N(E_F)$ is both higher than the value of 3.9 from [22] and the Cu 0:1 result but lower than the Cu FCC result. If we consider the overestimation of the Cu FCC $N(E_F)$ caused by the noise and a clear increase from the value of its parent structure Cu 0:1, we conclude that the $N(E_F)$ of bulk-like Cu is also increased. These observations of a decreased Nb $N(E_F)$ and an increased Cu $N(E_F)$ at the interface are in agreement with the literature. From figure 2 of Homma *et al* [11] and figure 2 of Banerjee *et al* [5, 23] the multilayering can be seen to decrease the $N(E_F)$ of Nb, which can be explained as an effect of broadening [11]. A higher Cu $N(E_F)$ is a possible explanation for the increased spin-lattice relaxation rate found by Yudkowsky *et al* [24] in Cu NMR experiments on an Nb/Cu ML. However, they speculate that the atoms in the central Cu layers have a higher $N(E_F)$ and the interface Cu layers have a lower $N(E_F)$. Yudkowsky *et al* also mention that a higher $N(E_F)$ for Cu is consistent with the expansions observed for the interlayer distances. Schuller (unpublished) speculates that this is due to electron transfer from Nb to Cu layers. We find electron transfer from Nb to Cu but this is a clear interface effect, as must be concluded from extrapolation to larger layer thicknesses. This implies that, if the latter speculations are correct, Cu must have a higher $N(E_F)$ at the interface.

The total $N(E_F)$ of the Nb/Cu 3:3 ML is given in the bottom row of table 2. It is somewhat lower than the weighted average of the $N(E_F)$ values of Nb and Cu of Moruzzi *et al* [22].

4.3. Total energies

In this subsection we study the total and layer-resolved energies of the incoherent system and the energies of the coherent BCC and FCC systems. The energies for the different systems in the mRyd/atom relative to the energies of the bulk metals, -7631.657 Ryd for Nb BCC and -3304.756 Ryd for Cu FCC, are given in table 3.

Table 3. Energies in mRyd/atom.

| | |
|--------------|-----|
| Total incoh. | 12 |
| Nb bulk-like | -23 |
| Nb interface | -20 |
| Cu interface | 47 |
| Cu bulk-like | 13 |
| NbCu FCC | 35 |
| NbCu BCC | 47 |

The energy in the first line in table 3 is obtained from the difference between the total energy of the incoherent system and nine times the Nb energy plus twelve times the Cu energy, divided by 21, the total number of atoms in the incoherent unit cell. The layer-resolved energies are average values for the atoms per layer. For most atoms the deviations from these average values are only a few mRyd. The largest deviation occurs in the Nb interface layer, with a difference of 6 mRyd. The value for NbCu FCC is the minimum of energy ΔE_0 in a parabolic fit of the three energy value differences ΔE for the FCC systems with the three different lattice parameter values a_{FCC} .

$$\Delta E = \Delta E_0 + \alpha(a_{\text{FCC}} - a_0)^2 \quad (1)$$

where $\alpha = 0.4280$ and $a_0 = 3.9042$ Å. The minimum energy and lattice parameter values ΔE_0 and a_0 are close to the values of the system where a_{Cu} is increased by 10%, which are 37 mRyd/atom and 3.971 Å. Evidence for an energy minimum between the 2% and 10% systems has already come from the hydrostatic pressure [25] value that changes sign on going from the 2% to the 10% system and it is very small for the 10% system. The hydrostatic pressure value of the NbCu BCC with a lattice constant a_{Nb} was already small so we performed no further calculations for this system.

The energy of the incoherent ML is 12 mRyd higher than that of the corresponding bulk parts. The origin of this energy raise can be seen from the four subsequent rows in table 3. From these we learn that the Nb atoms in both layers of the ML are about 20 mRyd more stable than the elemental Nb atom. In contrast, the Cu atoms have an energy that is higher than that for bulk Cu. As the total increase in the Cu energy is larger than the total decrease in the Nb energy and as there are more Cu atoms than Nb atoms per layer the incoherent Nb/Cu 3:3 ML is higher in energy than the combined energies of the bulk metals. Significantly, the bulk-like Cu atoms are 34 mRyd lower in energy than the interfacial Cu atoms which is the right trend. For larger layer thicknesses the innermost layers should behave as real bulk. The similarity of the energies of the Nb layers in the ML and the variation in the energies of the Cu layers is in line with observations made for the layer-resolved DOS curves of the ML. Again, the structural differences between the open Nb BCC (110) layers and the close-packed Cu FCC (111) layers are believed to be the cause of this.

Let us now consider the total energies of the coherent systems. These calculations were carried out to investigate the possibility of coherent Nb/Cu multilayers for small Λ . The Nb/Cu FCC and Nb/Cu BCC systems, which are both pure interface systems, have an energy that is higher than the sum of the Nb BCC and Cu FCC energies. Their values are also larger than the energy of the incoherent system. The increase in the energy of the incoherent ML with respect to the bulk metal energies must be due to the interface only as we found differences of less than 1 mRyd between the energies of the undisturbed elements and the 1:0 and 0:1 structures. With the Nb-Cu interface already raising the total energy, the structural energy costs to provide registry between the lattices of the Nb and Cu atoms raises the energy of the multilayers even further. This high energy for the coherent multilayers is evidence for the combined effect of the positive interaction energy and the structural energy costs.

5. Conclusions

Despite the fact that only partial commensuration is possible between FCC (111) and BCC (110) layers, the incoherent Nb/Cu 3:3 cell we have found is quite satisfactory. The DOS curves and the energies of Nb (1:0) and Cu (0:1) in the slightly deformed structure of the constructed ML compare well with those of pure Nb and Cu. The total energy differences are even smaller than 1 mRyd.

The ML total DOS can be considered to be a combination of broadened elemental DOS curves. For Cu the broadening is found only at the Nb/Cu interface. For Nb both the interface and the bulk-like layer are broadened by the multilayering which reflects the more open nature of the BCC structure. The DOS at the Fermi level shows a behaviour similar to that found in experiments. The broadening causes the Nb DOS at E_F to decrease [11] and a slight increase is found for the Cu DOS at E_F in the ML [24].

The total energy that is calculated for the incoherent ML makes it clear that the energy contribution of the interface interaction to the total energy is positive. A negative interaction energy could have counterbalanced or overcome the structural energy costs of forming a coherent ML, leading to possible coherent multilayers for small modulation wavelengths as was found for the Nb/Zr system [9, 26]. Coherent Nb/Cu multilayers in which, besides a positive interface interaction, there is also necessarily a positive structural energy contribution, are therefore excluded on the basis of our total energy results. In fact, one could speculate that the order-disorder transition, observed at a Λ of about 20 Å when decreasing Λ , is an indication that even for the smallest Λ Nb tries to retain its BCC [110] structure and Cu tries to stay FCC [111] modulated. Then, due to the large lattice mismatch and the interdiffusion, disorder for small Λ becomes understandable.

Acknowledgment

This work is part of the research programme of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

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